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TO THE STUDY OF THE LUNAR SURFACE

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GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 3.50

Microfiche (MF) _____

ff 653 July 65

Paper presented at the
SYMPOSIUM ON THE INTERPRETATION OF LUNAR PROBE DATA . II
Huntington Beach, California
January 26, 1968

N68-15975

FACILITY FORM 602

(ACCESSION NUMBER)

(THRU)

(PAGES)

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

APPLICATIONS OF LUMINESCENCE TECHNIQUES
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Raymond T. Greer, Vladimir Vand and
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Although luminescent emission from most materials is complex, the application of optical fluorescence as a complementary tool for the characterization of lunar and planetary materials has been advanced by newly developed, quantitative, non-destructive analytical techniques. Several specimens, likely to occur on the lunar surface, have been selected to demonstrate the variety of information that can be obtained. Variations in the intensity and wavelength in the fluorescence spectra of natural materials can be correlated with chemical composition, and the distribution of individual mineral components in a multi-phase assemblage is readily made apparent. An advantage of exploiting optical fluorescence lies in its ability to provide quantitative data for specimens of microscopic size.

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INTRODUCTION

Optical fluorescence spectra from many of the rock-forming minerals contain information of value to a variety of investigations of both macroscopic and microscopic polymineralic assemblages. Spectral analysis is non-destructive and can be used along with other techniques to study valuable extraterrestrial samples. Specific applications to the types and sizes of lunar and planetary materials anticipated, both on the surface and eventually available to the terrestrial laboratory, have been chosen to represent and to demonstrate how the complexities of the luminescent phenomena can be beneficial. The variations in color and intensity of the luminescent response can facilitate positive identification of mineral grains, singly or in bulk rock specimens, when a particular color (single or multiple emission band) is associated with the mineral or phase whose luminescent properties have been evaluated.

EXPERIMENTAL RELATIONS CONCERNED WITH PREDICTING THE NATURE OF LUMINESCENT EMISSION

The sensitivity of a luminescent inorganic solid to changes of composition, structure and atomic interactions can be an advantage in preliminary surveys for useful indigenous lunar resources. In addition,

the age of the mineral, its mode of formation, thermal and radiation treatment and other specialized problems¹ can be computed under favorable conditions .

The criteria for the effective utilization of optical fluorescence are based on extensive laboratory research on both natural and synthetic inorganic solids. The majority of natural minerals exhibit luminescent response that has been highly characterized by synthetic materials; the exceptions are few, and of minor importance here. Luminescent minerals can be considered natural phosphors, their analogues being the synthetic luminescent preparations; however, the natural solids usually exhibit zone fluorescence which is the effect of non-uniformity of the crystallization environment and of the trace element distribution. This difference constitutes an immediate analytical application in showing compositional zoning, emphasizing exsolution phenomena, or allowing the investigation of very small specimens, all of which make conventional separation and analysis by other techniques difficult, or in many cases, not possible. Other contributions of the techniques may include the qualitative identification of inclusions and the study of the segregation of impurities; the precise determination of phase equilibria and diffusion mechanisms; or the alteration by oxidation²⁻⁵ or reduction, and vacancy formation .

Correspondingly, investigating the luminescent response of phase assemblages comprising meteorites, establishes a representative basis to extrapolate present laboratory analyses, and the demonstrated interrelations of crystal hosts and luminescence activators, to the observations that can be recorded for other extraterrestrial specimens.

Although the nature of the activating electromagnetic or charged particle radiation necessary to stimulate luminescent emission can be critical ⁶⁻¹⁰ (for example, silicates are efficiently excited by 2537 Å radiation since the major absorption band for a silicate is near 3000 Å, whereas sulfides are responsive to 3650 Å radiation), moderate energy electron beams are preferred as proving more efficient and less damaging to sensitive specimens, than for example proton bombardment. In addition, many of the unique applications and experimental techniques described conveniently provide quantitative analytical information when the specimens are bombarded by electrons.

Photons and charged particles excite phosphors to different degrees of luminescence because of differences in penetration ranges, available energy per particle and particle densities, and excitation intensities. Photons lose energy immediately, and charged particles lose energy in small quantities. When the predominant anions

in a crystal are oxygen, both the specific host crystal and the activator can be important in determining if optical fluorescence will be excited by X-rays or by photons of lower energy.

It is also important to emphasize a general concept that the simple emission band locations and shapes of luminescent materials are determined by chemical composition and crystal structure, and are essentially invariant concerning the type or intensity of excitation. The spectral emission of both natural and synthetic phosphors is a function of the system parameters¹¹⁻¹⁴ listed in Table 1.

Table 1. Factors Influencing Spectral Distribution in Natural and Synthetic Inorganic Luminescent Solids

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1. Chemical composition, crystal structure, host crystal perfection
 2. Impurity concentrations, bond types, effective valences, coordination numbers, and locations in the solid
 3. Temperature of the solid during luminescence

These factors permit the effective use of luminescence as a diagnostic tool, in conjunction with other analytical methods, for purposes of identification as well as enhancing and contrasting small differences in such variables as composition.

A selection of typical silicates has demonstrated the potential lunar analytical applications; however, the principles and intricacies are valid for a large number of natural and synthetic phosphors. Correlations and contrasts will be indicated for the bulk specimens, powders and individual grains. All three forms of the specimens can be studied in detail utilizing a modified electron microprobe X-ray analyzer as a precisely controlled source of moderate energy electrons (30 keV), as well as applying the inherent analytical capabilities of the instrument.

The emissions from luminescent solids that are of immediate interest are X-ray fluorescence, conventional luminescence, and thermal radiation. The source of X-ray fluorescence is the electronic transitions in inner completed shells of atoms, yielding X-ray line spectra which are utilized in conventional electron microprobe X-ray analysis. The phenomenon of primary interest for the lunar surface studies is conventional luminescence which arises from two sources: 1. electronic transitions in inner incompleated shells of atoms, yielding the visible and near-infrared line spectra (typically the result of rare earth impurities in the solid), and 2. electronic transitions in outer shells of atoms, yielding visible and near-infrared band spectra (typical for the silicates that will be discussed). The thermal radiation is of minor interest here; the source is the

transitions of atoms vibrating and rotating, and electrons undergoing similar transitions mentioned above, yielding infrared band spectra.

CRYSTAL HOST AND ACTIVATOR

Numerous references provide compilations of the influence of activator ions in a variety of host crystals^{12, 15-17}. Of primary selenologic importance are the large number of oxygen-dominated host crystals, such as the silicates of Group II elements (Mg, Ca, Sr, Ba, Zn, and Cd). These exhibit a characteristic ultra violet and blue emission band of the complex host crystal anion (radical). This ultra violet and blue host crystal emission originates in the anion radicals (for example, in the SiO_4 tetrahedra in such orthosilicates as Mg_2SiO_4). When the silicates crystalize with about 0.01 weight % Mn, the longer wavelength green-to-red emission band is produced. The Mn-produced emission originates in cation sites (for example, Mn substituted Mg in magnesium silicate crystals).

Leverenz explains the host crystal luminescence process as an excitation transition involving electron transfer within an SiO_4 group from one of the four oxygen atoms to the central Si atom. The resultant

electron deficiency (positive hole) may then be exchanged among the tetrahedrally arranged oxygen atoms, until the excited electron on the Si atom makes a radiative return to one of the ligand oxygen atoms. By this model, the principal emitting atom would be an oxygen, although the entire SiO_4 group should be involved in the emission process.

Manganese in, for example, MgSiO_3 (magnesium metasilicate) produces new emission bands at the expense of the original bands of the host crystal. Incorporation of increasing proportions of Mn activator in MgSiO_3 steadily reduces the luminescence efficiency of the original 4200 \AA band of the host crystal, and produces a new emission band peaked near 6700 \AA . Also, higher Mn concentrations shift the red band to slightly longer wavelengths (0.15 to 6.2 weight % Mn). The 6740 \AA (peak) emission band of $\text{MgSiO}_3:\text{Mn}$ is attributed to transitions within Mn atoms (ions) substituted for Mg atoms (ions) in regular lattice sites. Similarly, the 6420 \AA (peak) band arises in the orthosilicate, $\text{Mg}_2\text{SiO}_4:\text{Mn}$. The original host crystal emission band in Mn activated silicates can be restored by incorporating Group IVB dioxides (for example, TiO_2 , ZrO_2 , HfO_2 , and ThO_2). The subsequent intensification of the original host crystal emission band represents an increase in cathodoluminescence efficiency. This intensification

would be associated with about 1 weight % of the impurities mentioned; otherwise the SiO_4 groups ($(\text{SiO}_3)_n$ chains for the metasilicate mentioned) are adequate to explain the short wavelength band.

The broad emission bands can be affected by temperature. In general, above 297 °K, the emission band will broaden without displacing its peak. Below this temperature range, the emission band will broaden and the peak will be displaced to longer wavelengths. For example, the luminescence spectrum of Mn-activated magnesium metasilicate at -180 °C consists of diffuse bands at 4450 and 5250 Å and a number of relatively narrow lines in the red between 6100 and 7000 Å, with a very strong line at 6410 Å. At room temperature $\text{MgSiO}_3\text{:Mn}$ exhibits a red luminescence which peaks near 6700 Å. Low temperature studies of the spectra and magnetic properties of excited and unexcited luminescent solids can provide information on bond types, effective valencies, and coordination numbers of the emitting atoms and the symmetries of the perturbed crystal fields surrounding the emitting atoms.

When impurities such as Fe or Ca are substituted in part for Mg in MgSiO_3 (for example), the luminescence efficiency of the system decreases, and a larger portion

of the energy of the incident excitant beam is manifested as heat, rather than optical fluorescence. In addition, the presence of impurity atoms can displace the original emission band.

CRYSTAL FIELD THEORY

An abbreviated discussion of the influence of the presence of divalent manganese in the silicate host crystals will clarify the parameters which determine the wavelength of the emission maximum in the 6000 - 7000 Å range, and will indicate how this can be useful in contrasting crystal structure and also the polymorphism of MgSiO_3 . The emission spectral displacements represent a sensitive indicator of structural variations since easily detectable 10 Å displacements correspond to approximately 0.01 ev, or less than 1 % of the energy difference between the excited and ground states involved in the radiative transitions. The crystal or ligand field theory^{19, 20} can be productively applied to explain the observed absorption and emission spectra.

²¹
White and Keester have concisely summarized the cogent terms and established concepts of crystal field theory as follows:

The d-electrons of transition metal ions are subjected to two sets of forces when the ions are incorporated in a crystal. First there is an

interelectronic repulsion between the various electrons in the orbital. This interaction is described by the Racah B-parameter. The interelectronic repulsion causes a splitting of the d-energy level into a sequence of levels in the gaseous free ion. Secondly, the ion in a lattice site is subjected to an electrostatic field from the coordinating anions. This electrostatic interaction, the "crystal field", causes a further splitting of the free ion levels. The number and arrangement of crystal field levels is determined by the electronic symmetry of the parent free-ion level and the geometrical site symmetry of the coordinating anions. The degree of splitting of the crystal field levels for each free-ion level is characterized by the crystal field splitting parameter, Dq . The observed electronic spectra of transition metal ions arise from transitions between the various crystal field levels, subject to certain selection rules.

Since there are two forces on the d-electrons there exists the possibility for either the interelectronic repulsion or the crystal field to be the dominant force. Respectively, these are the weak field and strong field cases. In the weak field case, the ground state has the same electronic symmetry and spin multiplicity as the free ion while at the strong field boundary there is a cross-over of levels and a different level becomes the ground state usually accompanied by a change in spin multiplicity which results in different selection rules and thus a totally different spectrum. A weak field usually implies tightly bound d-electrons with relatively little interaction with the coordinating anions while strong fields imply a high degree of interaction and thus covalent bonding. Ions of low charge coordinated by oxide anions are usually described by the weak field diagram. The energy level schemes described above can be computed in a general way for each d-electron configuration in terms of B and Dq . The calculated levels for octahedral coordination are known as Tanabe-Sugano diagrams (Tanabe and Sugano, 1954) and have been widely reprinted, being given in both general references cited above and in many other review articles.

The emitting level of divalent Mn is the ${}^4T_{1g}({}^4G)$ state. The variation in color emission from one phosphor to another depends upon the value of Dq and the ${}^6S - {}^4G$ separation appropriate to the environment of the divalent Mn ion. The chief color changes are due to changes in Dq . Further modifications of the color of the emitted light are produced by the band width in absorption and emission. When the space within the crystal available to the ion is decreased, the value of Dq increases, and the ${}^4T_{1g}$ state moves to lower energy .

EXPERIMENTAL

The luminescent response for several representative natural terrestrial, extraterrestrial (separated from meteorites) and synthetic silicates has been evaluated by studying the interrelationships of crystal host, activator, and impurity by discriminating the wavelength and intensity of the emission colors, the effect of impurities, polymorph present, and conditions of initial formation of the solid, both on a point-by-point basis (1-micron diameter) and by two dimensional color raster patterns at different wavelengths for the specimen surface. A modified Applied Research Laboratories EMX

microprobe X-ray analyzer facilitated the investigation of a number of cathodoluminescent phenomena, and permitted the assembly of quantitative information for bulk specimens, powders and detailed determinations for individual grains. The observed correlations and contrasts are consistent with the information previously discussed, and consequently provide a reasonable basis to expect useful information from studying the luminescent response and patterns that can be obtained from lunar surface specimens.

By coupling the standard analytical capabilities of a microprobe, the associated electronic display and recording systems, and monochromator-photomultiplier units, several specific types of information can be obtained; these are listed in Table 2.

Table 2. Microprobe Optical Fluorescence Information

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1. Recordings of optical fluorescence spectra; simultaneous monitoring of an element and the luminescent intensity with the monochromator set at a wavelength of interest
 2. Distribution of luminescent phases in specimens
 3. Relationships between fluorescence patterns and conventional X-ray representation of an area scan
 4. Relation of luminescent intensity to composition within a phase.

A diagram of the system appears in Figure 1, and
several review articles²³⁻²⁵ detail the conventional
analytical procedures in microprobe analysis.

Quantitative information can be obtained in digital
form, or photographically recorded as in the case of an
optical fluorescence display on an oscilloscope. The
oscilloscope displays correspond to color patterns,
over a narrow wavelength range of interest, generated
by the electron beam raster over the sample face, detected
and discriminated by the monochromator-photomultiplier
unit, and projected on the 10 cm x 10 cm oscilloscope
screen. This image is capable of representing a
minimum scan area of about 60 microns by 60 microns
of the sample face, when necessary.

The recording of optical fluorescence spectra
is accomplished by positioning the 1-micron diameter
electron beam (typically: 30 keV, 0.03 microamperes)
at a position of interest on an individual grain or
bulk specimen. The optical fluorescence is then
detected at the monochromator-photomultiplier unit.
By varying the monochromator settings, a complete
emission spectrum of the fluorescence can be displayed
on a strip-chart recorder. In addition, the option
exists to simultaneously record the luminescent

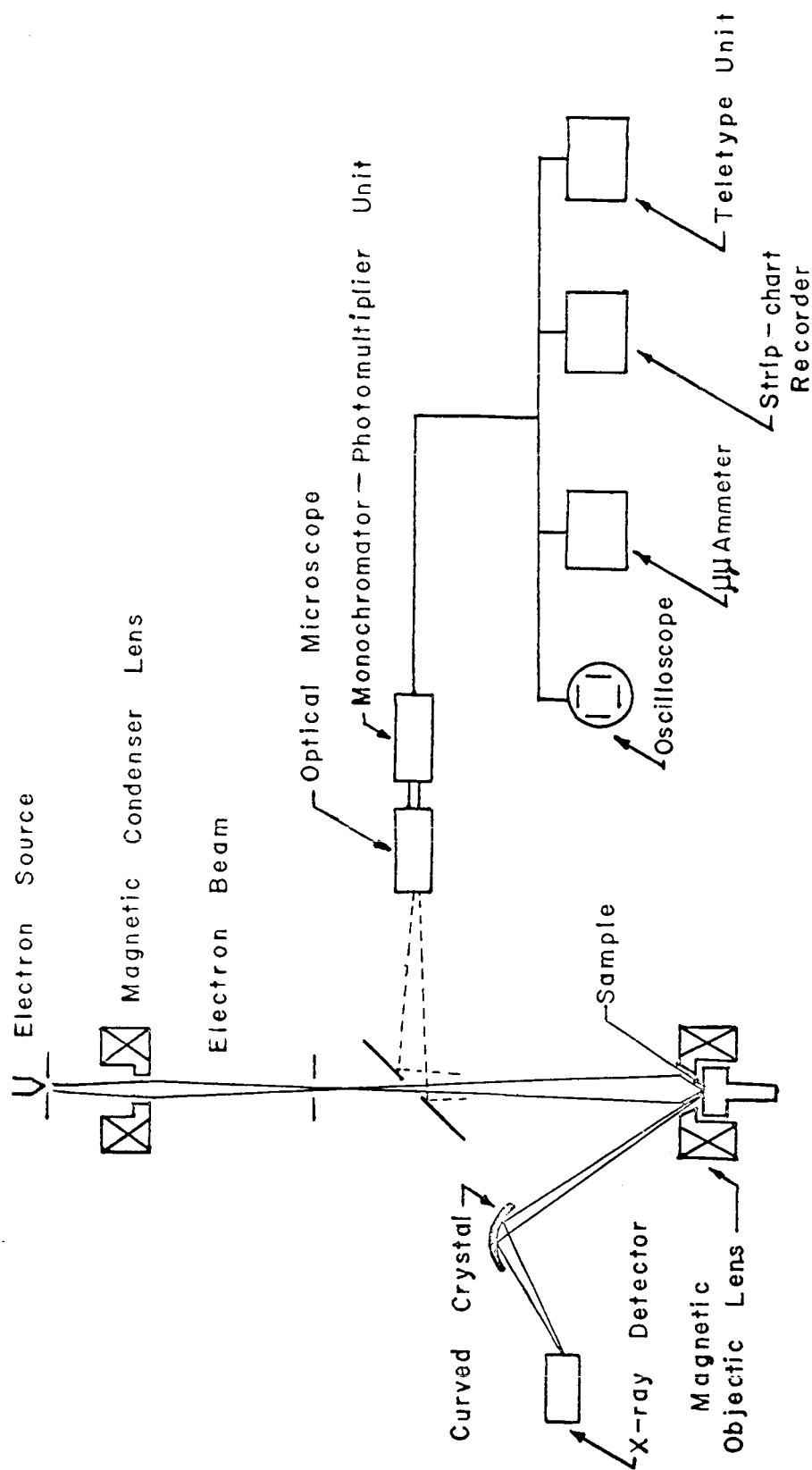


Figure 1. Cathodoluminescence Display System

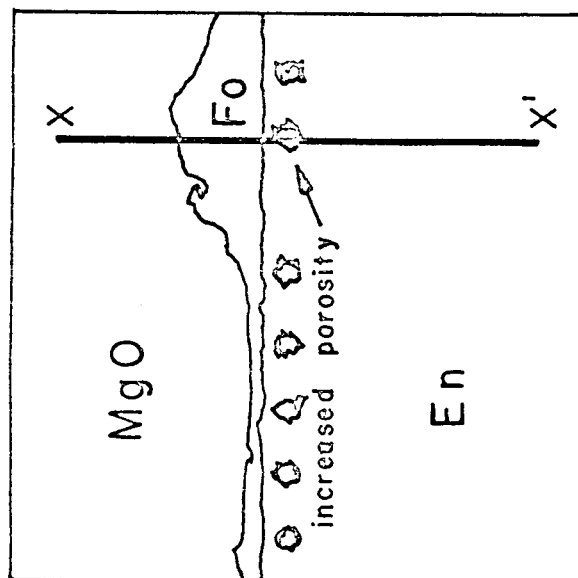
intensity (at a particular wavelength) and the presence of a particular element of interest on a dual-pen strip-chart recorder. In this case, the specimen is translated under the fixed electron beam so that both the optical fluorescence and X-ray fluorescence signal can be utilized. The characteristic X-ray lines for various elements are analyzed by means of three curved-crystal monochromators, and the composition of the sample is determined from the wavelength and intensity of these characteristic lines.

By sweeping the electron beam over a specimen surface and recording either the X-ray fluorescence or the optical fluorescence signal, an image can be constructed on a synchronized cathode ray tube, and photographed in less than one second. The area scanned ranges from about 60 microns x 60 microns to 200 microns by 200 microns. The patterns photographically recorded selectively delineate the emitting area of the specimen and permit comparisons of a particular color, intensity of that color, and any obvious associations with specific element distributions.

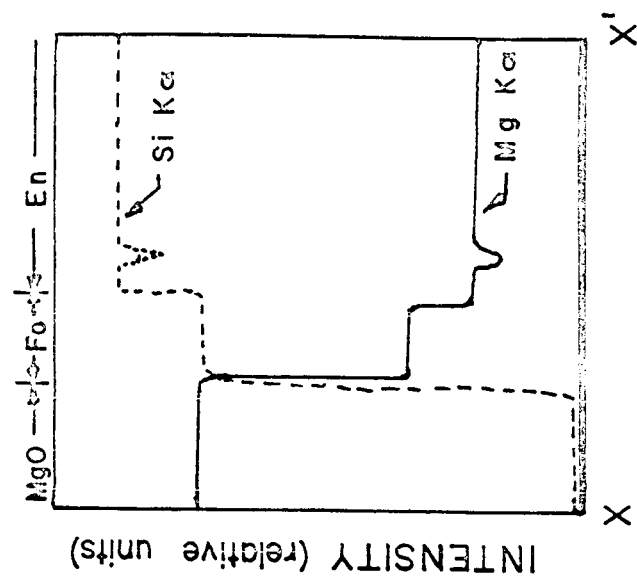
For purposes of correlation studies, the quantitative data is obtained by examining a number of 1-micron diameter positions on the specimen surface. The information is assembled by simultaneously recording the amounts of several elements present at that particular location and the luminescent intensity (at one monochromator setting). Multivariate statistical analytical techniques are then utilized to process the quantitative optical fluorescence and X-ray data collected from the bulk specimens, individual micron-size particles and of pre-selected micron-size areas of larger mineral grains. Thus, this nondestructive analysis can be applied to soil samples, and is of particular interest when the quantity of specimens available for analysis is limited.

RESULTS

In the case of bulk specimens, the luminescent analytical technique is especially suitable for studying co-existing phase assemblages, their reaction interfaces, and the reaction mechanisms. Figure 2 represents a reacted interface between two phases (for example, MgO and Enstatite, MgSiO_3), where a third phase has formed (Forsterite, Mg_2SiO_4). It has been demonstrated that the phase boundaries



(a)



(b)

Figure 2. Schematic diagrams of (a) reaction interface between MgO and En (enstatite) with the formation of Fo (forsterite), and (b) microprobe X-ray emission scan across X—X'. (Mg Kα —; Si Kα ---).

coincide exactly with those displayed by cathodoluminescence stimulation. In this example, the enstatite exhibited a lavender fluorescent color (5.0 RP 5/6)^{26,27}, the MgO a blue (5.0 PB 2/6), and forsterite a brick red (5.0 R 4/8). The forsterite formed within the original MgO, and along cracks and grain boundaries indicating a surface diffusion mechanism.

Individual enstatite grains were separated from meteorites, and quantities of these grains from the individual specimens were grouped side-by-side and stimulated to demonstrate the variation in color response from specimen to specimen. The blue-to-red and the varying shades of purple fluorescence are consistent with the relative position and intensity of the host crystal band (near 4200 Å) and the Mn-activated band (near 6700 Å) as discussed previously.

Studying individual grains appears to be the most promising in terms of quantity and quality of information that can be obtained by the luminescent analysis techniques. Under the electron bombardment, separate grains display large variation in fluorescence characteristics which are interpreted by the numerous relations presented previously. These variations are primarily attributed to differences in crystal structure,

host, activator concentration, and impurity level; in most cases, the influence of one of the variables overrides the others so that the differences are interpretable, and the contrasts useful in characterizing the particular specimen. For example, the trend of luminescent intensity for enstatite specimens separated from achondritic meteorites was usually greater throughout the visible portion of the spectrum as compared to that for enstatite specimens separated from chondritic meteorites. This general trend is associated with the greater purity of the achondrites, thus allowing a more efficient energy conversion to optical fluorescence. Also, the red luminescence observed is in agreement with both the concept of increasing the manganese concentration in the host crystal increases the intensity in the red emission region, while simultaneously decreasing the host crystal emission in the blue. The observed decrease in luminescent efficiency in going from an orthorhombic enstatite to a monoclinic enstatite specimen is consistent with the crystal field theory explanation concerning the environment of the atoms when the lattice spacing is altered, and also when there is a reduction in the site symmetry. In favorable cases, this type of information could be used to rapidly isolate high pressure phases in a mixture, and consequently

aid in establishing the pressure ranges experienced by the sample.

Examples of several of the effects are displayed in Figures 3 - 5. The photographs presented in these figures represent the kinds of information that can be monitored and recorded from an oscilloscope such as: 1. the quenching effect of Fe and Ca on luminescent emission (Fe: Figure 3a and 3b) (Ca: Figure 4), and 2. Mn as an activator, and exsolution lamellae (Figure 5a, 5b and 5c).

Figure 3a pictures the Fe distribution over a specimen surface obtained from the Abee clinoenstatite chondrite meteorite. By comparing Figure 3b, which represents the color display of 492 nm, the quenching effect of Fe is indicated. The dark areas in Figure 3b represent the effect of areas of high Fe.

Similarly, Figure 4 demonstrates the quenching influence of Ca. The photograph represents the color display of 621 nm for the Blithfield enstatite chondrite specimen, where the higher-Ca pyroxene and the lower-Ca pyroxene areas are contrasted by the lack of luminescent response for the higher-Ca areas.

In Figure 5a, the specimen current image outlines the specimen grain obtained from the Khairpur enstatite chondrite meteorite. Figure 5b indicates the blue, 491 nm, color distribution for the same grain. Figure 5c

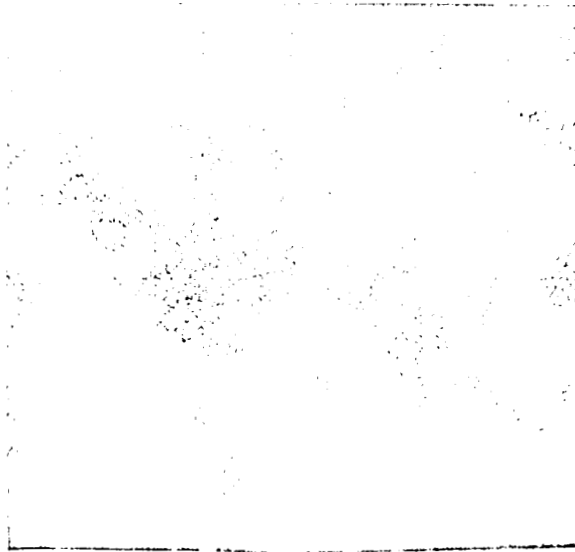


Figure 3a. Fe K distribution (Abbee meteorite:
200 microns x 200 microns).

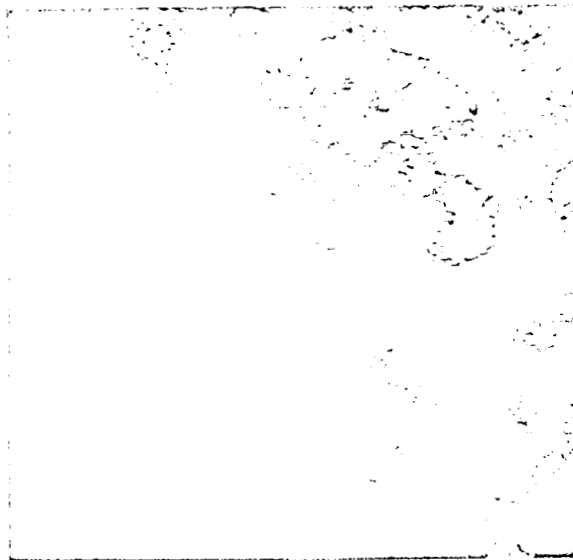


Figure 3b. 492 nm color display (Abbee meteorite:
200 microns x 200 microns).

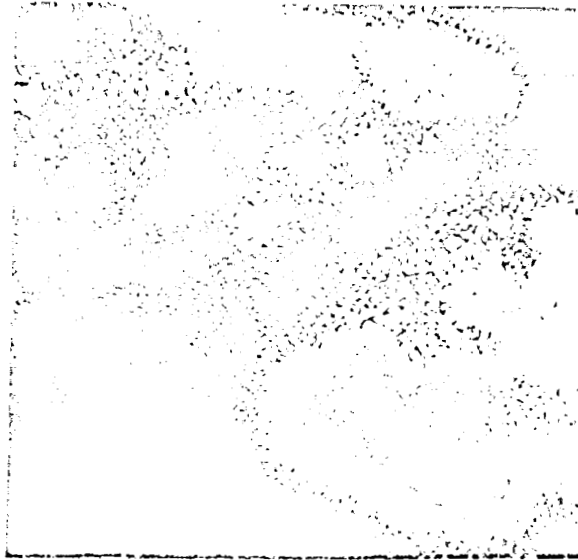


Figure 4. 621 nm color display (Blithfield meteorite:
200 microns x 200 microns).

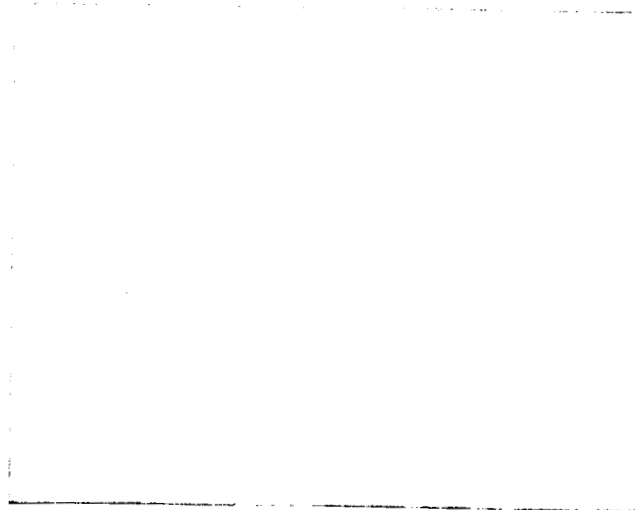


Figure 5a. Specimen current image (Khairpur meteorite: 200 microns x 200 microns).

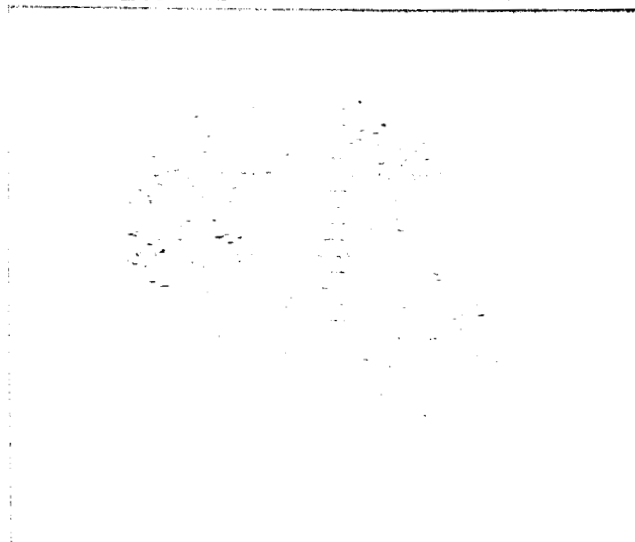


Figure 5b. 491 nm color display (Khairpur meteorite: 200 microns x 200 microns).

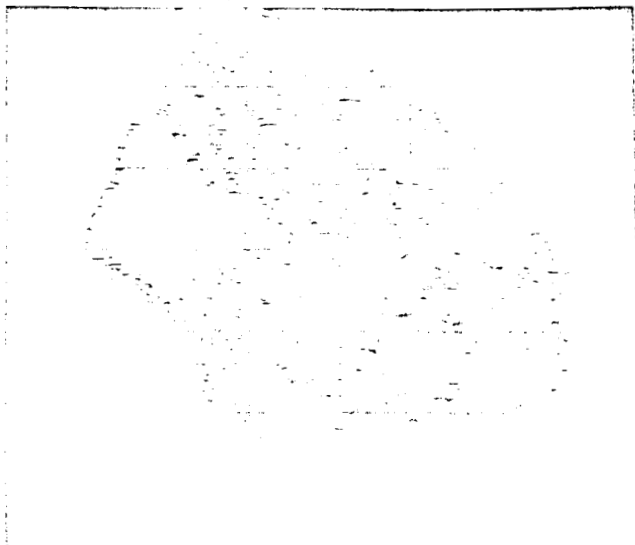


Figure 5c. 686 nm color display (Khairpur meteorite: 200 microns x 200 microns).

represents the 686 nm display, and emphasizes exsolution lamellae which would be difficult to detect for this specimen using other methods. In this sample, the higher-Ca pyroxene luminesces in the blue region of the spectrum, but not in the red. The low-Ca pyroxene is activated by Mn. The rhombic enstatite (low-Ca) and Ca-rich pyroxene solid solution are sharply contrasted, and establish a frozen in record of the temperature^{28,29} of equilibrium crystallization.

SCOPE OF FUTURE RESEARCH

Classification of materials into broad types through telescopic, in situ, or laboratory application of luminescence can be of considerable utility in the evaluation and eventual exploitation of indigenous resources. Such information may be applied in an effort to delineate the origin, character and arrangement of the lunar surface material profile, to reflect underlying formations, and to the understanding of the topographic conditions under which a lunar soil catena develops.

It will be of interest to evaluate the importance of the damage centers which are created in lunar surface material by exposure to long periods of irradiation.

In view of approaching solar maximum sunspot activity, it is to be expected that luminescence of

lunar rocks³⁰⁻³², as distinct from luminescence
of lunar gases, may be again observed, and the results
of this paper would have direct bearing on the
interpretation of the observations.

ACKNOWLEDGMENTS

Research reported in this paper was sponsored by the National Aeronautics and Space Administration under Contract No. NGR-39-009-015.

The authors wish to thank Dr. E. White for his assistance and suggestions during this research, and Dr. Brian Mason, Curator of Meteorites, Smithsonian Institution, Washington, D.C., for his help in securing sub-samples of meteorite specimens.

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